Experimental and kinetic analysis of the liquid phase hydrodeoxygenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran over carbon-supported nickel catalysts

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HIGHLIGHTS

- Kinetics of the hydrodeoxygenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran over Ni/C were investigated.
- 2,5-Dimethylfuran with 87% selectivity was produced from 5-hydroxymethylfurfural.
- Kinetic modeling indicates aldehyde hydrogenation as the rate determining step.

ARTICLE INFO

ABSTRACT

2,5-Dimethylfuran (DMF) is an attractive biofuel being stable, insoluble in water and an alternative to gasoline. DMF is accessible via hydrodeoxygenation of the cellulosic bio-based platform chemical 5-hydroxymethylfurfural (HMF). Efficient transformations of HMF to DMF have been reported to date; however, the kinetics of the reaction and a comprehensive analysis of the reaction network have not been addressed yet. In the present work, a plausible reaction network based on kinetic study of the hydrodeoxygenation of HMF over a carbon-supported nickel catalyst is proposed. The study of the reaction network showed the reaction indeed proceeds via the hydrogenation of the aldehyde group of HMF to form 2,5-bishydroxymethylfuran (BHMF) and subsequent conversion of BHMF to 5-methylfurfurylalcohol (MFA) followed by hydrogenolysis of MFA to DMF. Side reactions include the formation of 2,5-dihydroxymethyltetrahydrofuran (DHMTHF) and 2,5-dimethyltetrahydrofuran (DMTHF). A suitable kinetic model enabled estimating the kinetic parameters in the reaction temperatures range of 150–190 °C. Kinetics analysis revealed the hydrogenation of HMF to BHMF as rate-determining step, while subsequent deoxygenation to DMF proceeds faster. Interestingly, most undesired reactions were kinetically hindered under selected reaction conditions allowing high selectivity to the target product DMF.

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1. Introduction

The conversion of lignocellulosic biomass to liquid fuels and platform chemicals has been widely investigated in recent years (Dimitratos et al., 2009; Li et al., 2017; van Putten et al., 2013; Zheng et al., 2017). Biomass-derived molecules have the advantage of being obtained from the renewable feedstock and don't contribute to the global warming since the CO_2 emissions produced can be reabsorbed by plants during the photosynthesis

(Resasco et al., 2011). Especially the bio-based furan compounds have received considerable attention in both research and chemical industry. Among different furan-type chemicals, 5-hydroxymethylfurfural (HMF) is believed to be outstanding because it retains all six carbon atoms that were present in the hexoses substrate and can be produced with high selectivity from fructose. HMF presents a highly promising building block for a number of applications such as producing monomers for polymers, pharmaceuticals, agrochemicals, flavors and fragrances, macrocycles, and heterocycles. Additionally, it can serve as a precursor of fuel components. Under hydrogenation/hydrogenolysis, HMF can be transformed to the liquid fuel 2,5-dimethylfuran (DMF). DMF has a

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Nomenclature

BHMF	2,5-bishydroxymethylfuran
C_i	concentration of i-th species, mol m^{-3}
DHMTHF	2,5-dihydroxymethyltetrahydrofuran
DMF	2,5-dimethylfuran
DMTHF	2,5-dimethyltetrahydrofuran
D_{eff}	effective diffusivity, m^2 s^{-1}
G-L-S	three phase system gas-liquid-solid
HD	2,5-hexanedione
HMF	5-hydroxymethylfurfural
i	compound

$k_{n,app}$	apparent reaction rate constant of n-th reaction, lumped parameter including the intrinsic rate constant as well as adsorption constants, s^{-1}
l	characteristic size of a particle, m
MF	5-methylfurfural
MFA	5-methylfurfurylalcohol
n	reaction number
r_{eff}	effective reaction rate, mol m^{-3} s^{-1}
THF	tetrahydrofuran
η	effectiveness factor
φ	Thiele Modulus

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number of attractions as a biofuel. It exhibits an energy density 40% greater than that of ethanol making it comparable to gasoline (petrol). It is also chemically stable and, being insoluble in water, does not absorb moisture from the atmosphere.

Some studies have reported carbon-supported Pd, Pt and Ru as catalysts for HMF hydrogenation (Chatterjee et al., 2014; Chidambaram and Bell, 2010; De et al., 2012; Hu et al., 2014; Jae et al., 2014, 2013; Luo et al., 2015a, 2015b, 2016a, 2016b; Nishimura et al., 2014; Thananatthanachon and Rauchfuss, 2010; Zhang et al., 2012). Yields of DMF around 100% can be achieved using i.e. Pd/C and supercritical carbon dioxide – water condition (Chatterjee et al., 2014). Bimetallic catalysts such as Pd/Zn/C (Saha et al., 2014), RuSn/C (Gallo et al., 2013), CuRu/C (Binder and Raines, 2009; Kazi et al., 2011; Roman-Leshkov et al., 2007), PtCo/C (Wang et al., 2014) were also investigated, allowing good yields of DMF in the range of 46% (Gallo et al., 2013) - 98% (Wang et al., 2014). Other types of support materials applied for the synthesis of supported noble metal catalysts for HMF hydrogenation comprehend e.g. Pd/Fe$_2$O$_3$ (Scholz et al., 2014), ruthenium containing hydrotalcite catalysts (Mg/Al) (Nagpure et al., 2015) and Ru/Co$_3$O$_4$ (Zu et al., 2014), respectively. Typically, the catalysts integrated with noble metals are more efficient and selective for hydrogenation of HMF, they are stable and easy to handle. On the other hand, the cost and long term availability of such catalysts are their major drawbacks.

Nevertheless, base metal catalysts represent attractive alternatives. Kong and coworkers (Kong et al., 2014) reported the use of Raney-type metals (Cu, Co and Ni) to catalyse the hydrogenation of HMF. Using Raney Ni, a switchable synthesis of DMF and 2,5-d ihydroxymethyltetrahydrofuran was achieved with high yield of 96% and 88.5% respectively. The main reaction intermediates were 2,5-bishydroxymethylfuran (BHMF), 5-methylfurfural (MF), 5-methylfurfurylalcohol (MFA) and the main by-products of DMF production were 2,5-dimethyltetrahydrofuran (DMTHF) and 2,5-d ihydroxymethyltetrahydrofuran (DHMTHF). Depending on the reaction temperature, the main products of the reaction were either DMF or DHMTHF at 180 °C and 100 °C, respectively. Huang et al. (2014) developed a Ni-W$_2$C/AC catalytic system for the conversion of HMF to DMF. The DMF yield was reported to be as high as 96%. The main intermediates were BHMF, MF and MFA, and the main by-product was DHMTHF. Yang et al. (2015) studied Ni/Co$_3$O$_4$ for the catalytic conversion of HMF to DMF facilitating 76% yield of DMF under relatively mild reaction conditions. Kong and coworkers (Kong et al., 2015) achieved a DMF yield of up to 91% using a Ni-Al$_2$O$_3$ catalyst derived from hydrotalcite-like compounds.

In summary, several promising catalyst systems for selective production of DMF have been reported. However, despite these studies on the catalyst development, a comprehensive analysis of the reaction network together with identification of rate

determining steps have not been addressed yet. In the present work, we aimed to investigate the transformation of HMF to DMF over the supported nickel catalyst here Ni/C. Moreover, the kinetics of HMF hydrogenation over Ni/C was studied to elucidate the reaction network and key reaction intermediates. The effect of mass transfer on the formation of DMF was evaluated and throughout data evaluation provided kinetic parameters at different reaction temperatures gaining insights on major factors governing product selectivity.

2. Experimental

2.1. Preparation of Ni/C catalyst

Ni/C catalysts containing different amounts of metal loading were prepared by incipient-wetness impregnation. For example, to prepare 15 wt% Ni/C 3.8 g of nickel (II) nitrate hexahydrate Ni (NO$_3$)$_2$·6H$_2$O was added into water to yield a total volume of 4.3 mL in the beaker. The solution was stirred to prepare an impregnation stock solution. Then the metal-containing solution was dropwise added to the catalyst support (4.5 g of the activated carbon dried at 120 °C) under continuous mixing. The volume of the prepared stock solution was the same as the pore volume of the used activated carbon. The sample was then dried at 120 °C overnight, followed by reduction in a horizontal furnace under H$_2$ flow (8 L h^{-1}). The temperature of reduction was raised to 400 °C with the rate of 3 °C min^{-1} and kept at this temperature for 2 h.

2.2. Experimental procedure

All experiments were carried out in 50 ml stainless steel batch autoclaves equipped with a sampling valve. Batch autoclave is a conventional instrument that is extensively used to obtain the time course data, to do the reaction network analysis and kinetic studies (Nauman, 2007). Typically, the autoclave was loaded with 4.29 mmol of HMF, 26.8 mg of Ni/C and 30 ml of tetrahydrofuran (THF). The reactor was flushed 3 times with hydrogen prior to pressurizing to 100 bar hydrogen pressure at room temperature. The autoclave was then heated to a temperature ranging from 150 °C to 190 °C and operated at a pressure range of 100–140 bar for 2 h. During the reaction the mixture was stirred with a magnetic stirrer at 900 rpm. At various time intervals liquid samples were taken, filtered through a 45 μm PTFE filter prior to analysis and then analyzed off-line using a GC instrument (FOCUS GC by Thermo Fisher Scientific Inc.) equipped with a FID detector and high polarity bonded wax column Agilent J&W CP-Wax 57 CB. Essential parameters of GC analysis were the following: injection volume 1.0 μL, inlet temperature 250 °C, detector temperature